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## The structure of the blue luminescent $\delta$ -phase of tris(8-hydroxyquinoline)aluminum(III) (Alq<sub>3</sub>)

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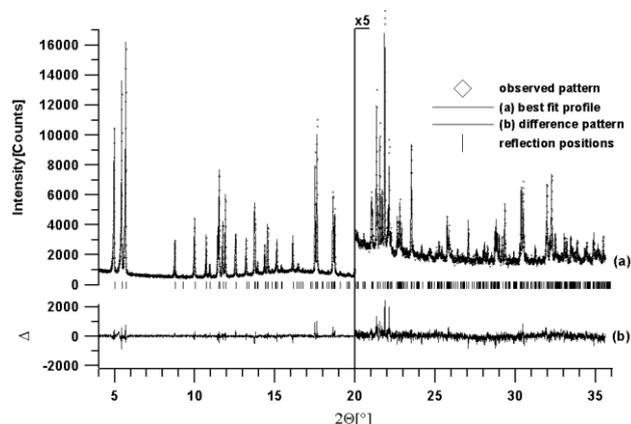
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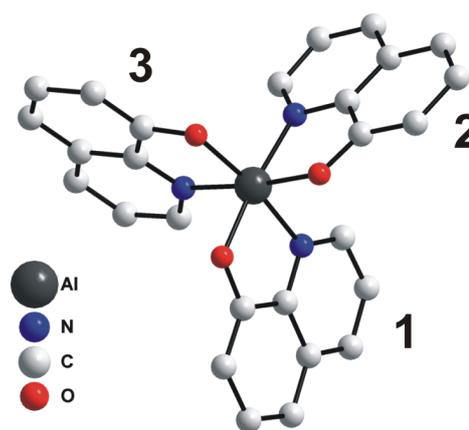
The existence of the facial isomer in the  $\delta$ -phase of Alq<sub>3</sub> is proven by x-ray structural analysis, revealing that both the different molecular structure and the weaker overlap of the  $\pi$ -orbitals of hydroxyquinoline ligands belonging to neighboring Alq<sub>3</sub> molecules as compared to other phases ( $\alpha$ ,  $\beta$ ) are likely to be the origin of the significantly different optical properties of  $\delta$ -Alq<sub>3</sub>.

Alq<sub>3</sub> is a stable metal chelate complex that can be sublimed to yield thin films and stands as one of the most successful materials used in organic light emitting devices for display applications. Although the partly nanocrystalline character of evaporated films used in these applications was known,<sup>1,2</sup> so far comparatively few investigations have been devoted to the crystalline state of this material.<sup>3,4</sup> A still unresolved issue concerns the isomery of the Alq<sub>3</sub> molecule. It is well-known that octahedral complexes of the type MN<sub>3</sub>O<sub>3</sub>, where M is a trivalent metal and N and O stand for the nitrogen and oxygen atoms in the hydroxyquinoline ligands, can occur in two different geometrical isomers: meridional and facial.<sup>5-7,20</sup> For the latter one quantum chemical calculations predict a larger energy gap which would result in a blue-shift of the fluorescence.<sup>5,7</sup> However, until recently all existing phases ( $\alpha$ ,  $\beta$  and  $\gamma$ ) have been found to consist of the meridional isomer.<sup>3,8</sup>

In a previous publication we have reported a new crystalline phase of Alq<sub>3</sub> ( $\delta$ -Alq<sub>3</sub>) exhibiting strongly blue-shifted fluorescence.<sup>4</sup> Its significantly different optical properties have been tentatively discussed in terms of the isomery of the Alq<sub>3</sub> molecule. Vibrational analysis supported the assumption of the facial isomer in  $\delta$ -Alq<sub>3</sub>,<sup>9,10</sup> but from all methods used so far (e.g. photoluminescence, infrared- and Raman measurements) it was not possible to distinguish clearly between intermolecular and intramolecular origin of the blue-shift. Very recent studies of the thermal and structural properties of Alq<sub>3</sub> gave more insight in the



**Fig. 1.** Scattered X-ray intensity for  $\delta$ -Alq<sub>3</sub> at ambient conditions as a function of diffraction angle  $2\theta$ . Shown are the observed patterns (diamonds), the best Rietveld-fit profiles (line) and the enlarged difference curves between observed and calculated profiles in an additional window below. The high angle part is enlarged by a factor of 5, starting at  $20^\circ$ . The wavelength was  $\lambda = 1.15 \text{ \AA}$ .



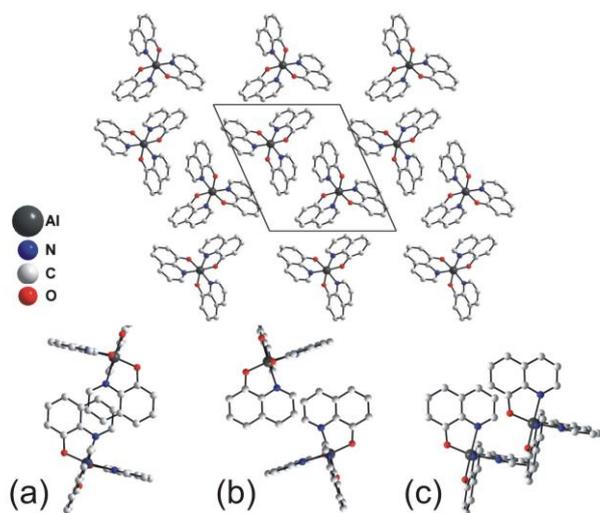
**Fig. 2** Alq<sub>3</sub> molecule of the  $\delta$ -phase with the three hydroxyquinoline ligands labelled with 1, 2 and 3.

forming properties of the different phases, identifying a phase transition at about  $385^\circ\text{C}$  to be the origin for the formation of  $\delta$ -Alq<sub>3</sub>.<sup>11</sup> Thus we are now able to produce pure powder of  $\delta$ -Alq<sub>3</sub> without significant admixture of other phases in larger amounts by annealing  $\alpha$ -Alq<sub>3</sub>, e.g. for 6h at  $390^\circ\text{C}$ . It has therefore been possible to obtain well-resolved powder diffraction spectra using synchrotron radiation as shown in Figure 1.

The unit cell<sup>†</sup> obtained is different from that published by Braun et al. as in their samples some admixtures of other phases have been present giving 4 peaks instead of 3 peaks at low diffraction angles, which has lead to a wrong indexing.<sup>4,11</sup> We note that the unit cell volume for  $\delta$ -Alq<sub>3</sub> of  $1072.38 \text{ \AA}^3$  is nearly the same value as reported for the  $\beta$ -phase of Alq<sub>3</sub>,<sup>3</sup> however, lattice parameters and angles are significantly different for the  $\delta$ -phase.

A global optimization method in direct space using simulated annealing followed by Rietveld refinement resulted in the crystal structure shown in Figure 3.<sup>†</sup> From the high quality of the refinement with a R-wp value of 6.5% as shown in the difference pattern in Figure 1, there is strong evidence that the  $\delta$ -phase consists of the facial isomer of Alq<sub>3</sub> shown in Figure 2. Refinement under the assumption of the meridional isomer resulted in a distorted molecule, whereby the distance for one coordination bond (Al-N) was elongated compared to the isolated molecule and a 9% worse Bragg R value was obtained ( $R^2=10.5\%$  facial,  $19.4\%$  meridional).<sup>††</sup> From these results  $\delta$ -Alq<sub>3</sub> is a nearly pure phase of the facial isomer.

In our former work, based on vibrational analysis by IR and Raman measurements, the significantly blue-shifted photoluminescence and the reduced intersystem crossing rate, we suggested  $\delta$ -Alq<sub>3</sub> to consist of the facial isomer.<sup>4,9,10</sup> However, the structural analysis presented here is the first clear evidence for the facial isomer in Alq<sub>3</sub>. The structure of  $\delta$ -Alq<sub>3</sub> obtained from synchrotron powder diffraction measurements is shown in Figure 2 and Figure 3. The molecule is only slightly distorted reducing weakly its symmetry and the planes defined by the O and N-atoms, respectively, are parallel.<sup>†d</sup>



**Fig. 3:** Crystal structure of  $\delta$ -Alq<sub>3</sub> in a projection along the *c*-axis. (a), (b) and (c) are projections perpendicular to the planes of the hydroxyquinolineligands 1, 2 and 3, respectively, showing the overlap between ligands of neighbouring Alq<sub>3</sub> molecules.

Another factor is molecular packing in the crystal. Interestingly the molecules are arranged in a manner minimising the possible overlap of the  $\pi$ -orbitals between pairs of hydroxyquinolineligands belonging to neighbouring Alq<sub>3</sub> molecules as shown in Figure 3. As demonstrated by Brinkmann et al. the orbital overlap influences the optical properties and can explain shifts in the photoluminescence spectra of different phases of Alq<sub>3</sub>. Here the pyridine rings of antiparallel ligands 1 face each other with an interligand distance of 3.4 Å (Figure 3(a)). The partial overlap of the rings is smaller as compared to the other known phases<sup>8,3</sup> and the atoms are slightly displaced, further reducing the overlap of the  $\pi$ -orbitals. Figures 3(b) and 3(c) show the projection perpendicular to the planes of Ligand 2 and Ligand 3, respectively. The interligand distance is about 3.45 Å and these ligands do not overlap at all. Thus we find a strongly reduced  $\pi$ -orbital overlap of neighbouring ligands in  $\delta$ -Alq<sub>3</sub> as compared to the  $\alpha$ - and  $\beta$ -phase. As only one ligand of each molecule overlaps with a neighbored molecule there are no  $\pi$ - $\pi$  links generating an extended one-dimensional chain as reported for the  $\beta$ -phase, so the interaction is limited to two molecules. We believe that this packing effect together with the changed symmetry of the molecule are responsible for the large blue-shift of the photoluminescence by 0.2 eV, which is in the same range as predicted theoretically by Curioni et al. for the two isomers.<sup>5</sup> Due to its importance for applications such as organic light emitting devices (OLEDs), intense research has been performed on Alq<sub>3</sub>. The facial isomer has been searched for many years and now it is clearly identified in the  $\delta$ -phase of Alq<sub>3</sub>. Its different geometry, higher dipole moment and different electronic properties are expected to be of high relevance for film forming and transport properties and thus for the performance of OLEDs. With our simple preparation method it is now possible to obtain large amounts of pure facial Alq<sub>3</sub> for further measurements. In preliminary experiments we have successfully converted amorphous thin films of yellowish-green Alq<sub>3</sub> into films showing blue fluorescence.<sup>11,88</sup> Their application in OLEDs is under investigation.

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## Notes and references

† a) Crystal structure data of  $\delta$ -Alq<sub>3</sub>: triclinic unit cell, space group P-1,  $a=13.24116(11)$  Å,  $b=14.42446(12)$  Å,  $c=6.1768(4)$  Å,  $\alpha=88.5553(7)^\circ$ ,  $\beta=95.9230(6)^\circ$ ,  $\gamma=113.9332(5)^\circ$ ,  $V=1072.382(15)$  Å<sup>3</sup>,  $\rho_{\text{calc}}=1.423$  g cm<sup>-3</sup>,  $Z=2$ ,  $\mu=2.48$  cm<sup>-1</sup>. b) Devices for X-ray diffraction experiments: 2-circle Huber diffractometer at the SUNY X3B1 beamline at National Synchrotron Light Source, Brookhaven National Laboratory, USA, double Si(111) monochromator, Ge(111) crystal analyzer,  $\lambda=1.4982(2)$  Å, Na(Tl)I scintillation counter with pulse height discriminator,  $T=295$  K,  $4.0^\circ < 2\theta < 35.7^\circ$  in steps of  $0.005^\circ$   $2\theta$ , glass capillary of 0.7 mm diameter. c) Structure determination process: Data reduction and background modeling by using the GUMI program,<sup>12</sup> indexing with Visser,<sup>13</sup> peak profiles and precise lattice parameters were determined by Le Bail-type fits<sup>14</sup> using the programs GSAS<sup>15</sup> and FULLPROF.<sup>16,17</sup> Structure determination by a global optimization method in direct space<sup>18</sup> using the DASH program (CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK). Rietveld refinements<sup>19</sup> using GSAS led to agreement factors of  $R_p=0.05$ ,  $R_wp=0.065$ ,  $RF^2=0.105$ ,  $\chi^2=1.6$ , 357 reflections, number of variables 115, slack soft constraints for bond lengths, angles and the planarity of the functional hydroxyquinoline groups to stabilize the refinement. d) Further details on the crystal structure investigation as well as tables of crystallographic data, positional parameters, temperature factors as well as selected bond lengths and angles for  $\delta$ -Alq<sub>3</sub> are available as electronic supplementary information (ESI). See <http://www.rsc.org/suppdata/cc/...>\*

§ Measurements, simulated annealing and Rietveld refinements of samples prepared by sublimation method as described in Ref 4 (there called fraction 3) verified the data published by Brinkmann et al. for the  $\alpha$ -phase of Alq<sub>3</sub> including the spatial overlap of the  $\pi$ -orbitals of neighbouring molecules (ligands B/B').

++ Detailed data and tables of bond lengths crystallographic data, positional parameters, temperature factors as well as selected bond lengths and angles for the assumption of the meridional isomer are available as electronic supplementary information (ESI). See <http://www.rsc.org/suppdata/cc/...>\*

§§ We note that the facial molecule in the  $\delta$ -phase of Alq<sub>3</sub> converts mainly to the meridional molecule during evaporation onto unheated substrates or after dissolving it in polar solvents like chloroform. When stored at ambient conditions, however, the  $\delta$ -phase is stable for months.

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